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3,390,083

**POLYESTER ADDITIVES FOR HYDROCARBON OIL COMPOSITIONS AND PROCESS OF PREPARING THE SAME**

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No Drawing. Continuation-in-part of application Ser. No. 445,725, Apr. 5, 1965. This application May 6, 1966, Ser. No. 548,065

Claims priority, application France, May 11, 1965, 16,663

2 Claims. (Cl. 252—33.4)

**ABSTRACT OF THE DISCLOSURE**

Mineral lubricating oil containing as an antiwear agent a blocked polyester of ethylene glycol, a  $C_{36}$  dicarboxylic acid and alcohol, together with an alkaline earth metal sulfonate forms a lubricant suitable for lubricating upper cylinders of marine diesel engines.

This application is a continuation-in-part of Ser. No. 445,725 filed Apr. 5, 1965, now abandoned.

The instant invention relates to improving the antiwear properties of various normally liquid petroleum hydrocarbon compositions through the use of improved novel oil soluble polyesters which are prepared by a novel process. The liquid hydrocarbon compositions are those used in association with internal combustion engines both as fuels and as lubricants. The inhibition of wear or the lowering of wear through the use of the novel oil soluble polyesters, sometimes called anti-wear agents, is a decided factor to be considered for gasoline, kerosene, jet fuels, diesel fuels and other middle distillate oils as well as for lubricating oils, marine diesel cylinder oils, automotive lubricating oil, refrigerator oils, hydraulic oils and cutting oils. Those hydrocarbon oils which are used as fuels advantageously may contain small amounts of the herein described novel anti-wear agents for the reason that in the transporting and handling of fuel compositions, pumps are employed and the wear on these pumps is materially reduced if these compositions, which are normally employed as fuels, contain the anti-wear agents. In other words, the addition of these novel oil-soluble polyesters enhances the wear resistance of these oils when used in conjunction with moving parts in pumps or in internal combustion engines generally.

One particular use to which these novel additives is put involves their addition to those lubricating oils which are employed for the lubrication of the cylinder walls of diesel engines, particularly marine diesel engines, and are customarily referred to in the trade as upper cylinder diesel lubricants. In engines of this type there has always been a serious wear problem as between the pistons, piston rings, and the inner surfaces of the cylinder liners and, when it is realized that many diesel fuels contain as high as 2-4 wt. percent sulfur which tends to have a corrosive effect due primarily to the acids formed by the combustion of the sulfur, the problem of reducing wear in the upper portions of the combustion chambers of diesel engines becomes of considerable importance. Ordinarily, the lubricant must also be readily pumped through the forced lubrication system normally associated with marine diesel engines. In particular, it must be spreadable and wetttable on the pistons, the piston rings, and the internal surfaces of the cylinder and remain there under the pressures that the piston rings exert against the cylinder linings. The fuel and lubricants pumps in a marine diesel engine are also subjected to heavy wear so that any upper cylinder diesel engine lubricant, to be satisfactory for commercial use, must have good anti-wear

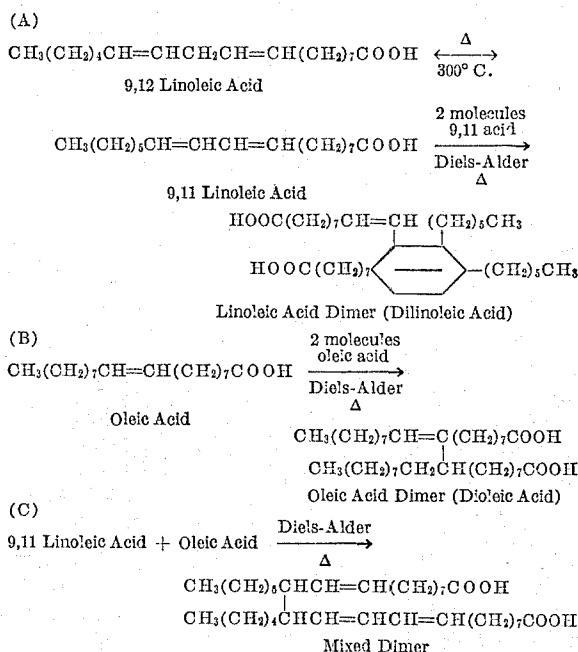
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properties for once the cylinder liners have worn more than 0.6% of their diameter, it is necessary that they be replaced at a cost of several thousand dollars per cylinder which is multiplied anywhere from 8 to 16 times for each typical marine diesel engine because there are that many cylinders in each engine. Lubricants which are useful from a wear standpoint should have a wear scar diameter of between 0.19 and about 0.35 mm. as measured in the Shell 4-ball wear test under relatively severe conditions of load versus times, i.e., under a 10 kilogram load at 1,800 r.p.m. for 1 hour at 77° F.

The novel polyester additive compounds which have the above-discussed desired properties of inhibiting or minimizing wear between frictional surfaces of metals are prepared from a polycarboxylic acid reacted with a glycol and alcohol, the alcohol blocking the free carboxylic acid groups.

The polycarboxylic acid is preferably a branched or straight chain, aliphatic dicarboxylic acid of 12 to 60 carbon atoms. Particularly, preferred are dimers of unsaturated fatty acids such as oleic and linoleic, the mixed dimer of linoleic and oleic acids and the dimer of dodecanedioic acid. It is also possible to employ the dimer of dicyclopentadiene dioic acid. While the foregoing acids are preferred, similar dicarboxylic acids such as "VR-1" described in U.S. 2,833,713 and "D-50" described in U.S. 2,470,849 may be used. The dioic or trienoic monocarboxylic acid, that is polymerized to give the dicarboxylic polymer, can have from 12 to 30 carbon atoms.

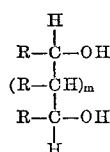
Commercial dimer acids discussed above are generally produced by polymerization of unsaturated  $C_{18}$  fatty acids to form  $C_{36}$  dibasic dimer acids. Depending on the raw materials used in the commercial process, the  $C_{18}$  monomeric acid may be linoleic acid or oleic acid or mixtures thereof. The resulting dimer acids may therefore be the dimers of linoleic acid, oleic acid or a mixed dimer of linoleic and oleic acid. Representative formulas of the foregoing monomeric and dimer acids may be illustrated as follows (it should be noted that the structure generally given for linoleic acid is that of 9,12-octadecadienoic acid but it is believed that prior to dimerization this acid isomerizes to the 9,11 structure, see in this regard the article "Dimer Acids," the Journal of the American Oil Chemists Society, vol. 39, December 1962, p. 535, J. C. Cowan):



It should be noted that the above structural formulas only indicate one of the several possible structural isomers. It is believed that the commercial dimer acids would contain mixtures of such structural isomers.

The dimer acid of linoleic acid with which one embodiment of the present invention is concerned is a C<sub>36</sub> dimer acid and is described in U.S. Patent 2,424,588, issued July 29, 1947, and entitled "Lubricant Composition," inventors: W. J. Sparks et al.

The glycol, or diol, used include those having the general formula:



wherein R is selected from the group consisting of hydrogen and an alkyl group having from 1 to 20 carbon atoms and wherein *m* is selected from the group consisting of 0 and 1.

It will be seen that these compounds are ethylene glycol or propylene glycols and their alkyl substituted derivatives. The preferred glycols are ethylene glycol and propylene glycol. The method of partially esterifying the glycol with the polymer of linoleic acid will be more fully hereinafter described.

The initially formed polymerized partial esters always contain one or more free carboxyl groups and at least one free hydroxyl group. The free carboxyl groups are reacted by esterifying them or blocking them with a monohydric alcohol containing from 1 to 6 carbons per molecule such as methyl alcohol or ethyl alcohol or by condensing and blocking the free carboxyl groups with a primary or secondary amine to form the corresponding amide derivatives. At least one free hydroxyl group per molecule remains. The amines employed can be the simple primary and secondary alkyl amines in which the amine nitrogen is attached to one or two C<sub>1</sub> to C<sub>6</sub> alkyl groups or a polyamine such as hexamethylene tetramine or hexamethylene pentamine are employed as the amine. The simple amines which are useful are mono or diethyl amine, mono or dimethyl amine, diisopropyl amine, isopropyl amine, methyl isopropyl amine, and the like.

The dimer of linoleic or oleic acid is customarily employed although some monomer and trimer are usually present in small amounts as an impurity in the dimer. These dimer acids are a commercial product and are sometimes referred to as a C<sub>36</sub> dimer acid, and are known in the art, e.g. see U.S. Patent 2,424,588. Generally speaking, the simple esterification of the dicarboxylic or dimer acid with the glycol is carried out using equimolar amounts of the two reactants, with the esterification being continuous, usually under refluxing conditions until more than one but less than 2 moles of water of reaction have been produced per mole of acid and per mole of glycol employed. By so controlling the reaction conditions, catalyst concentration, and the like, the polyesterification reaction results in a partial ester being formed. In general, it is desired to control the reaction when using equimolar portions of glycol and the acid so that between about 1.5 and about 1.9 moles of water are produced. The catalyst is a conventional one such as para-toluene sulfonic acid and the reflux conditions in benzene resulted in the use of a temperature of about 80° C. and about 95° C., a condenser and trapper used, the refluxing being stopped when the theoretical amount of water has been collected by azeotropic distillation with the benzene. Under these refluxing conditions, a time of reaction and refluxing of between about 2½ hours and 3½ hours will have been sufficient to collect the desired molar quantities of water to assure that only a partial esterification has been effected. It is, of course, apparent that some fully esterified product will be produced, the amount so produced is mini-

mized if a careful control and measurement of the amount of water collected is carried out.

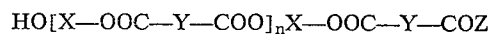
In carrying out the partial esterification, a hydrocarbon solvent such as benzene, toluene is refluxed while containing the equimolar amounts of the glycol and the dicarboxylic acid. Generally the reflux temperature will be in the range of 80–105° C. The reaction time will vary depending upon the degree of polymerization desired. Reaction times of between about 2 and about 12 hours may be used but the product should not be polymerized to such an extent that it becomes substantially insoluble in the hydrocarbon oil into which it is to be incorporated. The moles of water removed (a measure of the degree or amount of esterification) may be varied from between about 1.25 and about 1.95 but generally is within the range above stated, i.e., between about 1.5 and about 1.9 moles. This partial ester is hereinafter designated polyester A. The reacted mixture, maintained at the same or slightly lower temperatures, is then reacted with a C<sub>1</sub>–C<sub>6</sub> alkyl monohydric alcohol such as methanol or ethanol for from about 30 minutes to about 1 hour or at least for a sufficient length of time to insure that all remaining carboxyl groups of the A ester are blocked, i.e., esterified with the alcohol leaving as the desired final product the polyester B which is a polyester containing at least one unreacted hydroxyl group per molecule.

Depending upon the esterification conditions of time and temperature and the number of moles of water removed during the partial esterification, the degree of polymerization as well as esterification can be controlled so that in the following formula, *n* may have a value anywhere from 1 to 25 with the preferred *n* value ranging generally between about 1 and about 9. Generally, for an additive for use in connection with a marine diesel cylinder oil, the *n* value preferably is between about 5 and about 20 and for automotive lubricating oils of SAE 10 to SAE 30, *n* values are preferably between about 7 and about 25. For fuels such as kerosene, heating oils, or jet fuels, the additive employed should have an *n* value preferably of from about 3 to about 13. In order to produce a compound wherein *n* is about 25, it is necessary to form and remove from the esterifying mixture about 1.96 moles of water per mole of glycol and per mole of acid. The polymeric, partially-esterified composition is believed to have the general formula:



wherein X is the alkylene portion of from 2 to 20 carbon atoms of the glycol employed originally and Y is the alkylene portion of the acid and wherein *n* is an integer ranging from about 1 to about 25. Preferably *n* is between about 1 and about 9. The desired upper limit of *n* depends on the solubility limitation in the particular hydrocarbon oil in which the additive is to be incorporated.

The above-identified polymeric partial ester is then further reacted with ammonia, a primary or secondary amine under amidation conditions or with a monohydric alcohol such as methanol or ethanol in order to block the free carboxyl groups with an amino group by reacting the OH group of the free carboxyl radicals or by esterification with the alcohol. In other words, the carboxyl hydrogens in the above polymerized partial ester are replaced by an alkyl group of 1 to 6 carbon atoms which would be formed if a monohydric alcohol were employed or the OH of the carboxyl groups would be replaced by a NR'R'' wherein R' would be a C<sub>1</sub>–C<sub>6</sub> alkyl group or hydrogen, and R'' would be a C<sub>1</sub>–C<sub>6</sub> alkyl group or hydrogen, or the R's could be the residue of hexamethylene tetramine or hexamethylene pentamine or the like. The blocked ester would have the formula:



wherein Z is an —O alkyl, —NH<sub>2</sub>, —NH(alkyl) or —N(alkyl)<sub>2</sub>. At any event, the subsequent treatment to esterify or amidate the free carboxyl group blocks those

free carboxyl groups remaining in the polymeric partial ester from further reaction. Inert diluents such as heptane, benzene and toluene may be employed for the partial esterification and for the subsequent blocking esterification or amidation. The esterifying catalyst for forming the partial ester may be para-toluene sulfonic acid or any other conventionally employed catalyst such as concentrated sulfuric acid. The degree of esterification may be measured by a measurement of the acid value of the ester formed which should be between about 5 and about 80 mg./KOH/gram. This method of determining the degree of esterification is an alternate to the measurement of the moles of water collected.

The blocked polyesters so produced, as before described, are incorporated into the hydrocarbon oils or fuels in such amounts as to be soluble in the oils or fuels but, in any event, in an amount ranging between about 0.001 and about 5.0 wt. percent to produce useful anti-wear properties in the oil or fuel composition. Preferred amounts used are between about 0.01 and about 2.0 wt. percent. It is, of course, within the purview of the invention to use lesser amounts of blocked polyester but the anti-wear properties are usually substantially diminished. Within the limits of solubility in the hydrocarbon oils or fuels, greater quantities of blocked polyester may be employed but generally no increased anti-wear properties will result through the use of greater quantities. Oil concentrates to the limit of solubility may also be employed and marketed for use, being cut back to the desired level upon being added to the fuel or oil in sufficient amounts to give, in the final composition ultimately used, the range of amounts as above stated.

Particularly in the case of marine upper cylinder diesel lubricants, the use of the above-described blocked polyesters in hydrocarbon oils are preferred to be in association with so-called "over based" additives, e.g., organic salts such as alkaline earth metal salts of oil soluble sulfonic acids, salicylates, naphthenates and phenates which have been reacted with more than the stoichiometric proportions of metal base, for example, calcium or barium oxide or hydroxide and in which free calcium or barium carbonate or oxide remain in colloidal suspension therein. The novel blocked polyesters, when added to such hydrocarbon oils containing the "over based" compounds does not result in the formation of haze or precipitates.

These various types of "over-based" additives may more specifically be described as follows: The petroleum sulfonates generally used as lubricating oil detergents are the oil soluble alkaline earth metal salts of high molecular weight sulfonic acids which are produced by the treatment of petroleum oils of the lubricating oil range with fuming sulfuric acid and generally have molecular weights of about 300 to 700, e.g., 300 to 500. These petroleum sulfonates are well known in the art and have been described in numerous patents, e.g., U.S. Patent 2,467,176.

Another type of detergent additive which finds utility in the instant invention is the sulfonated alkylate bottoms prepared by mixing a feed composed of olefin polymers having from 9 to 18 carbon atoms, i.e., polymers of  $C_3$  or  $C_4$  olefins such tripropylene, tetrapropylene; polymers of butene-1 or butene-2; or copolymers of propylene with butene with a molar excess of benzene, toluene or the like which admixture of aryl hydrocarbon and olefin polymer is injected along with gaseous hydrogen chloride into a stirred reactor containing an aluminum chloride complex as a catalyst. After the alkylation reaction is completed, the contents of the reactor are conducted to a setting drum from which the separated hydrocarbon layer is drawn off, water washed, caustic treated to remove acidic components, and finally distilled into four fractions: (1) the unreacted aryl compound, (2) a light alkylate boiling from 200° to 530° F., (3) a detergent alkylate fraction boiling from 530° to 580° F. or as high as 605° F., and (4) the alkylate bottoms which boil above the end point of the detergent alkylate fraction.

These alkylate bottoms generally have an initial boiling point from about 580° to 605° F. and are the alkylate bottoms which are subjected to sulfonation in the same manner as above described with respect to the production of petroleum sulfonates. These sulfonated alkylate bottoms are likewise well known in the art. The production of the detergent alkylate bottoms is fully described in Hakala, U.S. Patent 2,886,609, patented May 12, 1959. Both the alkylated aryl sulfonates and the petroleum sulfonates are used in the form of their alkaline earth metal salts, i.e., their calcium or barium salts. Specific examples of the two types of sulfonates include: calcium petroleum sulfonate, barium petroleum sulfonate, calcium  $C_9$ - $C_{18}$  alkyl benzene sulfonate and barium  $C_9$ - $C_{18}$  alkyl benzene sulfonate.

The above sulfonates can be either neutral sulfonates, i.e., where the sulfonic radical is fully neutralized with an equimolar amount of alkaline earth metal compound, or the sulfonates may be of the so-called "high alkalinity" or "over based" type. In the latter case, additional metal base, i.e., BaO or CaO, in excess of that required for simple neutralization is incorporated and reacted with the sulfonic acid to form an alkaline product with free alkaline earth metal oxide in dispersion. This is then blown with carbon dioxide to convert the alkaline earth metal oxide into the corresponding carbonate. Recent work has indicated that such so-called high alkalinity sulfonates are nothing more than dispersions of neutral sulfonates and a carbonate of the alkaline earth metal used. These dispersions are believed to exist in the form of colloid sols.

The alkyl phenates are well known and are likewise useful in the hydrocarbon oils. The oil soluble alkaline metal and alkaline earth metal salts of these phenols contain from one to three alkyl groups per phenol group. The alkyl groups can be straight or branched chain and are generally from 5 to 20 carbon atoms per alkyl group, preferably 9 to 16 carbon atoms per alkyl group. These alkyl phenates may likewise be of high alkalinity or "over based." They are prepared by reacting the alkyl phenol or the corresponding sulfide with an excess of the alkaline earth metal basic compound again followed by neutralizing the basic product by blowing the same with carbon dioxide.

The synthetic detergent additive oil mentioned in the second paragraph of the following Example 1 is the "over based" sulfonated detergent alkylate bottoms as described above with respect to the method of producing the "over based" sulfonated alkylate bottoms. The active ingredient constitutes 56% of the "over based" bottoms and 44% of a convenient vehicle which is a light lubricating mineral oil.

The fuel and lubricating oil compositions of the invention can also include conventional fuel and lubricating oil additives in amounts ranging between about 0.001 and about 4.0 wt. percent, based on the weight of the total composition. Usually in gasolines and fuel oils the amount will range from about 0.001 to 1.0 wt. percent. Oxidation inhibitors such as phenyl-alkyl-naphthylamine, rust inhibitors such as sodium nitrite and lanolin, the aforementioned detergent additives, viscosity index improvers and pour depressants such as the polymethacrylates, dyes, sludge dispersants, etc. can be used. Additionally, naphthenic acids are useful as additives when employed in small amounts. These are derived from petroleum stocks and should preferably be obtained from fractions having a boiling range at least as high as the kerosene, diesel fuel, or lubricating oils in which they are incorporated. The most desirable naphthenic acids are those containing at least one cyclic nucleus of 4, 5 or 6 carbon atoms and containing one carboxyl group per nucleus. The preferred naphthenic acids have molecular weights of from about 250 to about 300 and neutralization or acid numbers of from about 150 to about 225.

## Example 1

2000 grams (3.5 moles) of dilinoleic acid and 212 grams (3.5 moles) of ethylene glycol were refluxed in 980 mls. of benzene in the presence of 15 grams of p-toluene sulfonic acid until 119 grams (6.6 moles) of water were removed, after 3 hours at a reaction temperature of 95° C. About 1.88 moles of water were formed and removed per mole of acid and glycol and *n* averaged about 8. Partial polyester A is thus produced and is so referred to hereinafter. The reaction mixture was cooled to a temperature of 75° C. and a solution of 35 grams of methanol in 75 grams benzene was added. The reaction mixture was refluxed for ½ hour at 83° C. and water removed by azeotropic distillation until a total of 129 grams (7.1 moles) of water over the total reaction period was thus removed. The polyester, as prepared in this example, was used in tests described in the examples and tables, hereinafter set out, and is referred to herein for convenience as polyester B.

Using polyester B gave deposits generally described as soft medium or soft slight on the pistons and as clear or slight as to the ports, while using the commercial oil gave deposits described as hard medium or soft medium, respectively, on the pistons and about the same or slightly more deposition than when using the polyester B oil, as to the ports.

As a further illustration, polyester A in its reaction mixture is condensed with 50 grams of ethyl amine in 80 grams of benzene and reacted under the same reflux conditions as set forth above when using methanol.

## Example 2

A series of CAV fuel pump bench tests were carried out by recycling fuel continuously for extended periods through a standard CAV N-type fuel pump to determine crank level wear when using a kerosene fuel with and

TABLE I.—CAV N-TYPE FUEL PUMP BENCH TEST

Time (hours).....	Crank Case Lever Wear (0.001 inch)				
	100	200	250	300	400
Fuel:					
Kerosene.....	3.4				
Auto diesel Oil.....			0.9		
Kerosene+0.1 wt. percent Polyester "A" <sup>1</sup> .....	Nil	0.5		0.8	
Kerosene+0.1 wt. percent Polyester "A" <sup>1</sup> +water <sup>2</sup> .....	2.0				
Kerosene+0.1 wt. percent Polyester "A" <sup>1</sup> +0.025 wt. percent Primene 81 R <sup>3</sup> +20 p.p.m. Arquad 2 HT <sup>4</sup> .....		Nil			
Kerosene+0.1 wt. percent Polyester "A" <sup>1</sup> +0.025 wt. percent Primene 81 R +20 p.p.m. Arquad 2 HT+water <sup>2</sup> .....			2.5		
Kerosene+0.1 wt. percent Polyester "B" <sup>5</sup> .....	Nil	Nil		Nil	Nil
Kerosene +0.1 wt. percent Polyester "B" <sup>5</sup> +water <sup>2</sup> .....	Nil	Nil		Nil	Nil

<sup>1</sup> Polyester "A" is the unblocked polyester ester of ethylene glycol and dillinoleic acid (Example 1).

<sup>2</sup> Kerosene plus 10 wt. percent water are well mixed for 1 hour, after which time the water is allowed to settle to the bottom and the kerosene saturated with water is used in the test.

<sup>3</sup> Surfactant—mixture of C<sup>18</sup>-C<sup>22</sup> straight chain alkyl primary amine.

<sup>4</sup> Surfactant—mixture of di(C<sup>14</sup>-C<sup>18</sup> alkyl) dimethyl ammonium chloride.

<sup>5</sup> Polyester "B" is a blocked polyester of ethylene glycol and dilinoleic acid in which the blocking group is CH<sub>3</sub> as prepared in Example 1.

Two grades of marine diesel upper cylinder lubricant compositions were made up for extensive use in diesel engines of more than a score of ocean going vessels while in commercial service. The oils used were of the following compositions:

Component	Oil A, SAE-40, wt. percent	Oil B, SAE-50, wt. percent
Synthetic detergent additive oil <sup>1</sup> .....	21	21
Polyester "B".....	1	1
Naphthenic Acids (Acid No. 180).....	1	1
Solvent extracted neutral naphthenic oil: 60 SSU at 210° F.....	54	
78 SSU at 210° F.....	23	44
Deasphalted naphthenic bright stock, 90 SSU at 210° F.....		33

<sup>1</sup> 56% sulfonated alkylate bottoms neutralized with CaO plus an excess of CaO, in suspension, carbonated, and 44% light lubricating mineral oil to give 300 total base number mixture, marketed as Bryton C-3JJ.

without the additive composition of the invention. The effect of water contamination was also determined.

It will be seen from the foregoing tests that the addition to kerosene fuels of blocked polyesters of the invention prevented crank lever wear, whereas, polyester A use showed far greater lever wear.

## Example 3

Table II shows the advantageous effects in reducing pump wear when the blocked polyesters of the invention are added to the naphtha fuels designated.

The following results illustrate the advantageous effects of polyester B in reducing pump wear when used in various naphthas compared with turbo-jet fuel in a Four Ball Test.

TABLE II.—FOUR BALL EXTREME PRESSURE TEST <sup>1</sup>

Polyester "B" in p.p.m.....			Nil	500	1,000	1,500	2,000
Naphtha Fuel	Boiling Range, °C.	Reid Vapor pressure at 100° C.	Load in Kg. to breakdown				
Medium virgin.....	41-159	6.6	42	57	66	74	82
Heavy virgin.....	146-185	0.9	42	47	54	59	59
Light virgin.....	25-153	17.2	20	39	46	52	52
Do.....	45-96	8.8	37	49	64	68	68
Turbo-jet fuel.....			56				

<sup>1</sup> Shell Four Ball Test—Manual for the Four Ball E. P. Lubricant Testing Machine, issued by Shell Petroleum Company Limited, P. D. & R. Department, Technical Division, Reference No. 29/52.

Both of the above formulations were blended at 160° F. and the solutions had a total base number of 60. After about 4000 hours of operation in each diesel engine, the pistons and the air intake and exhaust ports were examined for carbon and varnish deposits. For comparative purposes, some cylinders of the same engine were run on a commercially available upper cylinder lubricant which was free of the additive, polyester B.

## Example 4

Polyester B was evaluated in gasoline engine crank-case lubricant formulations and compared with zinc dialkyl dithiophosphate, the alkyl groups of which consisted of about 65% primary amyl and about 35 wt. percent of primary isobutyl radicals as an anti-wear additive. This material was prepared by reacting P<sub>2</sub>S<sub>5</sub> with a mixture

of 65 wt. percent primary amyl alcohol and 35 wt. percent of primary isobutyl alcohol and neutralizing with zinc oxide. Polyester B appears to be a more stable additive and one which does not contribute to engine deposits, e.g., undercrown deposits. The following base formulation was used and compared with two other samples of the same formulation, one containing polyester B and the other zinc isobutyl, amyl, dithiophosphate, respectively, in the Ford Zephyr Mk. III engine test (Ford Testing Schedule for Approval of Lubricating Oils, Ford Motor Company Limited, England).

Base formulation:	Vol. percent
Paraffin base oil, 140–160 SSU at 100° F. ....	86.22
V.I. Improver—copolymer of vinyl acetate, N-vinyl pyrrolidone, fumarate esters (32–37 wt. percent conc. in oil) .....	6.0
Detergent additive—sulphurized barium octyl phenate (60% conc. in oil) .....	4.2
Neutral petroleum—calcium sulphonate (36 wt. percent conc. in oil) TBN16 .....	2.08
Ashless detergent—polyisobutylene succinic acid reacted with ethylene diamine (amic acid) .....	1.5

TABLE III.—FORD ZEPHYR MK. III ENGINE TEST PERFORMANCE  
[Oil (base formulation above shown)]

Anti-wear additive (wt. percent)	Zinc isobutyl, amyl, dithiophosphate (1.0)	Polyester "B" (0.5)	Nil
Valve tip wear:			
Average (inch×10 <sup>-4</sup> ) .....	5	7.6	11.5
Range (inch×10 <sup>-4</sup> ) .....	2–10	4–14	6–18
Tappets .....	4 TP, 1 TS	All O.K.	2 TS, 1 S, 2 BS
Ring Sticking (max.=10):			
Cold .....	5.95	8.0	7.6
Hot .....	9.15	10.0	10.0
Pistons (max.=10):			
Outside Skirt Varnish .....	8.0	8.1	9.1
Outside Skirt Pick-up .....	10.0	8.3	10.0
Undercrown Lacquer .....	(1)	2.4	2.7
Undercrown Carbon .....		10.0	10.0
Gudgeon (Wrist) Pin Lacquer (max.=10) .....	3.7	3.0	3.0

<sup>1</sup> All covered by carbon.

TP=trace pitting, TS=trace scuffing, S=scuffing, BS=badly scuffed.

In terms of tappet wear, all six test tappets showed no wear using polyester B but zinc isobutyl, amyl, dithiophosphate additive gave incipient pitting and scuffing on 5 tappets out of six.

Ring sticking and undercrown cleanliness were both markedly improved with polyester B as compared with the dithiophosphate.

To determine the extent to which these results might be affected by the other additives in the blend, a third test was run using the same basic formulation oil but which did not contain an anti-wear additive (oil 3). As expected, valve train wear was significantly increased, but piston cleanliness was similar to that obtaining in oil 2 of Table III. These engine tests show that polyester B gives significantly lower tappet wear, together with improved engine cleanliness compared with the zinc isobutyl, amyl, dithiophosphate additive.

#### Example 5

The three oils of Table III were also tested in the Petter W-1 engine. The performance of oil 2, containing polyester B, gave a piston as clean as when new. This condition was duplicated by using control oil 3. The bearing weight loss in both cases was satisfactory. Oil 1

gave excellent bearing weight loss results but piston skirt and undercrown deposits were undesirable.

TABLE IV.—PETTER W-1 ENGINE TESTS

Oil .....	1	2	3
Bearing weight loss (mg.) .....	2.6	12.3	12.5
Piston Skirt Lacquer (10=clean) .....	9.0	10.0	10.0
Piston Skirt Interior .....	(1)	Clean	Clean
Undercrown .....	(2)	Clean	Clean
Oil ring rating, ring sticking .....	All free	All free	All free

<sup>1</sup> 2% light red stain.

<sup>2</sup> 75% black lacquer, 20% red lacquer.

#### Example 6

To further illustrate the invention, Example 1 is repeated but using 3.5 moles of dioleic acid, i.e. the dimer of oleic acid, in place of the 3.5 moles of dilinoleic acid used in Example 1.

What is claimed is:

1. A lubricant for marine diesel engine upper cylinders suitable for use in engines operating on high sulfur fuel oil, consisting essentially of a major amount of a mineral lubricating oil, and as an anti-wear agent, about

1 wt. percent dissolved in said oil of a blocked polyester having the formula:



wherein X is an ethylene group, Y is a C<sub>34</sub> group of a C<sub>18</sub> dimer acid, n is about 5 to about 20, and R is a C<sub>1</sub> to C<sub>6</sub> alkyl group, and a detergent amount of an over-based alkaline earth metal sulfonate lubricating oil detergent additive.

2. A lubricant according to claim 1, wherein R is methyl, said alkaline earth metal is calcium, and said sulfonate is derived from alkylated aryl bottoms.

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